

LETTER

Discreditation of diomignite and its petrologic implications

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ABSTRACT

Diomignite ($\text{Li}_2\text{B}_4\text{O}_7$) is discredited as a mineral species, and this discreditation has been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification. Diomignite was originally reported to occur in virtually every crystal-rich inclusion in spodumene from the Tanco pegmatite in southeastern Manitoba, Canada. However, detailed study of 30 randomly selected crystal-rich inclusions in the purported type material deposited at the U.S. National Museum of Natural History, 30 inclusions in the purported type material from the American Museum of Natural History, and several hundred inclusions in self-collected samples reveals that diomignite is absent in every inclusion examined. Because no holotype specimen exists and no neotype sample was provided by the surviving authors of the original description, the presence of diomignite could not be validated. The evidence provided in the original description to the IMA in 1984 is shown to be insufficient to support the existence of diomignite as a mineral species.

The previously reported boron-rich (12 mass% B_2O_3) composition of the melt represented as crystal-rich inclusions in spodumene and petalite from the Tanco pegmatite was predicated on the assumption that diomignite is a common daughter mineral that occurs in most inclusions and that the inclusions are primary melt inclusions. The nonexistence of diomignite, and the absence of other borate daughter minerals, in these crystal-rich inclusions indicates that the boron content was greatly overestimated and so comparisons to experimentally generated boron-rich (>10 mass% B_2O_3) boundary-layer melts are unwarranted. Furthermore, the discreditation of diomignite negates the inferred role of a $\text{Li}_2\text{B}_4\text{O}_7$ -flux-rich melt in the generation of primary pegmatite textures and rare element oxide mineralization in the Tanco pegmatite.

Keywords: Diomignite, discreditation, pegmatite, inclusions, boron, internal evolution

INTRODUCTION

London et al. (1987) reported diomignite ($\text{Li}_2\text{B}_4\text{O}_7$) as a new mineral from the Tanco pegmatite in southeastern Manitoba, Canada. It was the first mineral species to be described solely as a daughter mineral in fluid inclusions, following approval in 1984 (IMA 84-58) by the International Mineralogical Association, Commission on New Minerals and Mineral Names, currently Commission on New Minerals, Nomenclature and Classification (CNMNC). Detailed examination of several hundred spodumene-hosted inclusions from the Tanco pegmatite shows that the evidence presented in the original description of diomignite is insufficient to warrant valid mineral species status. Discreditation of diomignite was officially approved by the CNMNC in January 2016 (decision 15-H). This paper reviews the lines of evidence presented in the original description and calls into question the origin of the crystal-rich inclusions (London 2008), the estimated composition of the entrapped fluid (London 1986), and the inferred role of a $\text{Li}_2\text{B}_4\text{O}_7$ -flux-rich melt in the internal evolution of the Tanco pegmatite (London 1985, 1986) and the alteration of the wall rocks (Morgan and London 1987; London 2008).

OCCURRENCE

Diomignite was reported to be part of an assemblage of daughter minerals that includes albite, cookeite, quartz, pollucite-analcime solid solution, a microlite-group mineral and an unidentified carbonate mineral within spodumene-hosted fluid inclusions from the Tanco pegmatite, Manitoba, Canada. According to London et al. (1987):

Diomignite has been observed only as small ($\leq 30\ \mu\text{m}$) anhedral to euhedral crystals in fluid inclusions in spodumene, and tentatively in fluid inclusions in the petalite from which most of the spodumene formed. In these associations, diomignite is an abundant and widely distributed phase; it occurs in virtually every crystal-rich inclusion in spodumene.

However, examination of several hundred of the same type of inclusions in self-collected samples, and in 30 crystal-rich inclusions in samples deposited as type material at the U.S. National Museum of Natural History, and in 30 inclusions in samples deposited as type material at the American Museum of Natural History, shows that most inclusions contain only quartz, zabuyelite, cookeite, and a low salinity aqueous or aqueous carbonic fluid (see supplemental material¹). Despite an exhaustive search, no inclusions were shown to contain crystals of lithium tetraborate.

Thomas and Davidson (2010) reported a second occurrence

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¹Deposit item AM-16-75757, Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to <http://www.minsocam.org/MSA/AmMin/TOC/>).

of diomignite in beryl-hosted fluid inclusions from the Muiane pegmatite, Mozambique, but referred to the compound as $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$. However, the Raman spectrum used to identify this phase does not match the spectrum of anhydrous $\text{Li}_2\text{B}_4\text{O}_7$ (Paul and Taylor 1982). The reported vibrational frequencies ($390, 446, 544, 1028, 1097, 1352 \text{ cm}^{-1}$), however, closely match $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$. Rainer Thomas (personal communication 2015) has since retracted this report. The Raman spectrum of the phase reported as $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ was not saved by Thomas and Davidson, and R. Thomas was unable to obtain a duplicate spectrum from the same beryl-hosted inclusions. The report of diomignite or a hydrated lithium tetraborate in the inclusions from the Muiane pegmatite should therefore be disregarded.

TYPE MATERIAL

Material purported to be type specimens of diomignite was deposited in the Smithsonian Institution, National Museum of Natural History (USNM 164236), Washington, D.C., and the American Museum of Natural History (AMNH 98989 and 98990) in the form of doubly polished wafers of spodumene from the Tanco pegmatite (London et al. 1987). These representative samples of spodumene were believed to be replete with diomignite-bearing inclusions (London et al. 1987). However, these samples were not used to characterize all of the properties reported in the original description and therefore cannot be regarded as true type specimens. Because no true holotype, or co-type, sample of diomignite exists, a request for a neotype specimen was made in the proposal for discreditation. No neotype specimen was produced by the principal author of the original description.

OPTICAL PROPERTIES

Table 1 in London et al. (1987) lists the refractive indices $\omega = 1.612(1)$ and $\epsilon = 1.554(2)$ obtained from synthetic lithium tetraborate crystallized at 600°C and $200 \text{ MPa } P_{\text{H}_2\text{O}}$. However, only an averaged refractive index of $n \approx 1.6$ is reported for diomignite. According to London et al. (1987), diomignite is readily recognized in doubly polished plates of spodumene by its high birefringence, and where diomignite and an unidentified carbonate mineral coexist, the carbonate usually can be distinguished by its higher birefringence. However, about 3% of spodumene-hosted inclusions contain two or more crystals of zabuyelite (e.g., Fig. 1) that commonly display different relief and retardation due to differences in their thickness and orientation within the inclusion. Raman spectroscopic analyses of several hundred high-birefringence daughter minerals in the spodumene-hosted fluid inclusions indicate that they are zabuyelite, or very rarely calcite or nahcolite.

MORPHOLOGY

Morphological and optical properties are among the main features used to identify solids in unopened fluid inclusions. According to London et al. (1987), euhedral crystals of diomignite commonly appear as pseudorhombic or pseudocubic forms. However, when crystal drawings of zabuyelite are generated by SHAPE (Dowty 2000) using only simple first-order pyramids and prisms, and are viewed down the *c*-axis, the crystals display pseudo-cubic or pseudo-hexagonal outlines (Figs. 2a and 2b, respectively). It is therefore suggested that zabuyelite, a common and widespread daughter mineral in spodumene-hosted inclusions

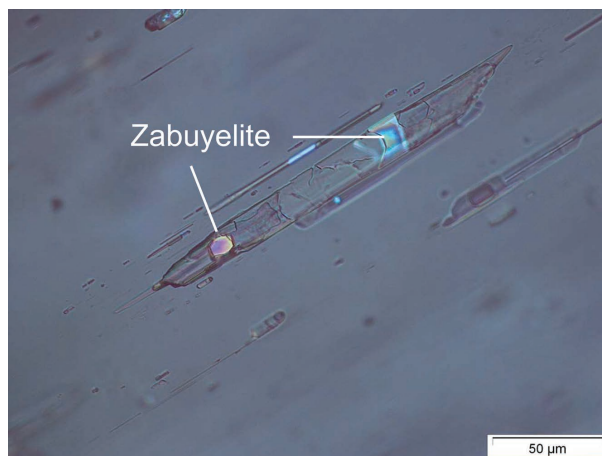


FIGURE 1. Photomicrograph of a spodumene-hosted inclusion in the type sample AMNH 98090 viewed under crossed polarized light. The inclusion contains two zabuyelite crystals that display different relief and retardation due to differences in size and orientation. (Color online.)

(Anderson et al. 2001), was misidentified by London et al. (1987) as diomignite. The only SEM image of a crystal purported to be diomignite is shown in London et al. (1987, Fig. 1c). However, the illustrated sample was not submitted as type material, and therefore could not be analyzed by Raman spectroscopic or electron microprobe techniques.

CHEMICAL DATA

London et al. (1987) unsuccessfully attempted to chemically analyze daughter crystals they believed to be diomignite using a SIMS microprobe. Even though modern microanalytical techniques such as EMPA, SIMS, and LA-ICP-MS are now used for quantitative analysis of boron and lithium, a chemical analysis of diomignite has still never been made. The presence of Li, B, and O was inferred by London et al. (1987) on the basis of filtered energy-dispersive analysis of daughter minerals in opened fluid inclusions. The detector employed at the time of the original description was incapable of detecting light elements (i.e., $Z < 11$) and the spectra obtained by London et al. (1987) showed no X-ray emission lines, indicating the mineral consists wholly of elements with an atomic number of less than 11. This evidence is consistent with zabuyelite (Li_2CO_3), which consists wholly of light elements.

X-RAY DIFFRACTION DATA

Single-crystal structure data were not provided in the original description. According to London et al. (1987), confirmation of the identity of diomignite was based on two faint Gandolfi X-ray diffraction patterns. The studied crystal could not be reexamined and was not included as type material because, as reported in London et al. (1987), it “had popped off” the glass whisker mount and was lost. Eleven of the X-ray diffraction lines obtained from the lost crystal closely match the powder XRD lines obtained from synthetic $\text{Li}_2\text{B}_4\text{O}_7$ crystals synthesized at 600°C and $200 \text{ MPa } P_{\text{H}_2\text{O}}$ (London et al. 1987). However, without the original daughter crystal, or the XRD pattern of a suitable replacement of known provenance, the XRD evidence presented by London et al. (1987) does not pass sufficient rigor to be regarded as unambiguous.

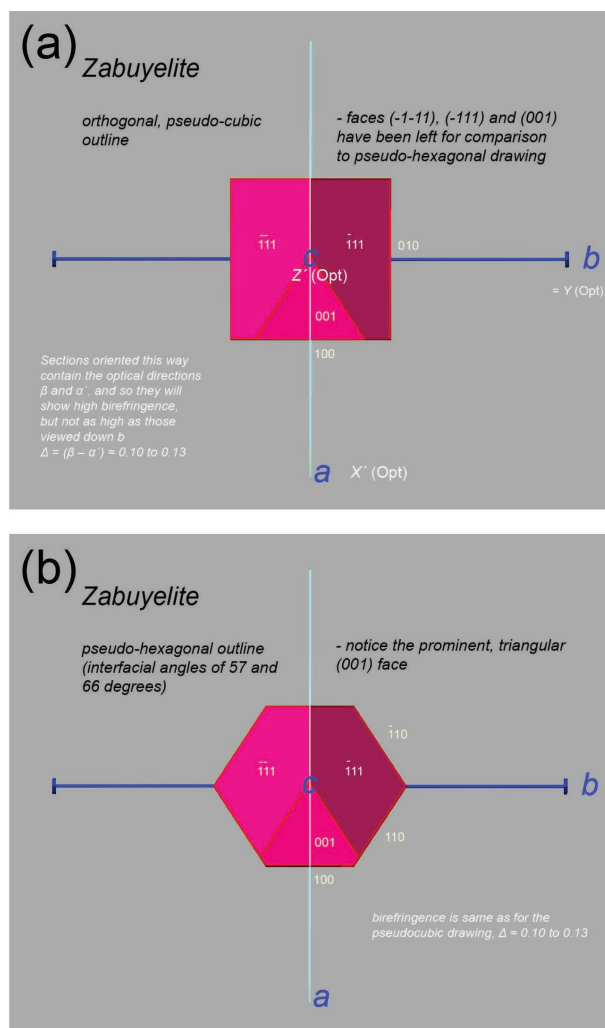


FIGURE 2. (a) Pseudo-cubic outline of zabuyelite when viewed down the *c*-axis. (b) Pseudo-hexagonal outline of zabuyelite when viewed down the *c*-axis. (Color online.)

SOLUBILITY DATA AND PHASE RELATIONS

According to London et al. (1987), diomignite can be distinguished from carbonate minerals in fluid inclusions by differences in solubility. The carbonate phase is said to dissolve between 275 and 300 °C while diomignite is said to dissolve at a temperature of about 420 °C. In most inclusions, however, the carbonate phase (i.e., zabuyelite) persists well above the liquid-vapor homogenization temperature (ca. 312 °C) to various temperatures of inclusion decrepitation (>400 °C). This indicates that the delimiting solubility evidence used in the original description is incorrect.

If solid lithium tetraborate did exist in an aqueous fluid inclusion, it would most likely occur as a hydrated species. According to the investigations of Dukelski (1906), Reburn and Gale (1955), and Touboul and Bétourné (1996), the stable lithium borate in the system $\text{Li}_2\text{B}_4\text{O}_7\text{-H}_2\text{O}$ at low temperature is $\text{Li}_2\text{B}_4\text{O}_7\cdot 3\text{H}_2\text{O}$, not anhydrous $\text{Li}_2\text{B}_4\text{O}_7$.

London (1986) suggested that phase relations in the synthetic system $\text{LiAlSiO}_4\text{-NaAlSi}_3\text{O}_8\text{-SiO}_2\text{-Li}_2\text{B}_4\text{O}_7\text{-H}_2\text{O}$ are closely

analogous to the natural fluid represented by the inclusions in spodumene from Tanco. However, this comparison does not take into account the effect that Li_2CO_3 , a major component, exerts on the microthermometric behavior of the inclusions. Any broad similarities in phase relations between the zabuyelite-bearing inclusions and the modeled synthetic system $\text{LiAlSiO}_4\text{-NaAlSi}_3\text{O}_8\text{-SiO}_2\text{-Li}_2\text{B}_4\text{O}_7\text{-H}_2\text{O}$ must therefore be regarded as coincidental.

Heating silicate-rich fluid inclusions under confining pressure will normally produce a liquid that can be quenched to glass plus an aqueous solution regardless of the origin of the contained solids (i.e., daughter mineral, alteration phase, or accidentally trapped mineral) (Bodnar and Student 2006). The contents of some crystal-rich inclusions in spodumene may be melted and then quenched to form glass beads plus aqueous fluid, but this is not unequivocal evidence that the daughter mineral assemblage represents the products of an entrapped silicate melt.

RAMAN SPECTROSCOPIC ANALYSIS

The application of Raman microprobe to the analysis of fluid inclusions was described by Rosasco and Roedder (1979). Although in situ Raman spectroscopic analysis is an effective technique for identifying borates in unopened fluid inclusions (e.g., Peretyazhko et al. 2000; Thomas and Davidson 2010), it was not employed in the description of diomignite in 1984. In this study, Dilor X-Y and LAB RAM HR microprobes were, respectively, used to collect spectra from crystal-rich inclusions in the type samples, USNM 164236 and AMNH 98090 (see supplemental material¹), and from several hundred inclusions in self-collected samples (Anderson et al. 2001).

Twenty-nine of the thirty inclusions examined in AMNH 98090 contain an assemblage of minerals consisting of quartz, zabuyelite, and a phyllosilicate (cookeite). The phyllosilicate found in most inclusions occurs as thin sheets or plumose aggregates (e.g., S98090-4e in the supplemental material¹) and its Raman spectrum displays a weak band at 266 cm^{-1} (e.g., B98090-15b supplemental material) and OH stretching at about 3638 cm^{-1} .

IMPLICATIONS

The discussion above indicates that the evidence presented in the original description of diomignite is circumstantial, incorrect, or equivocal, and is insufficient to warrant mineral species status. Because (1) the type material was improperly designated, (2) true type material does not exist, and (3) a neotype sample was not furnished, the identity of the mineral described by London et al. (1987) could not be validated. The discreditation of diomignite has significant implications for the interpretation of the crystal-rich inclusions in petalite and spodumene and the model proposed by London (2008) for the internal evolution of the Tanco pegmatite.

The Tanco pegmatite is among the largest and most highly evolved pegmatites known and has been the subject of numerous studies over the past 57 yr (e.g., Hutchinson 1959; Wright 1963; Crouse and Černý 1972). The model proposed by London (2008) to explain the cooling history and internal evolution of the Tanco pegmatite is based on fluid inclusion, phase equilibrium, and experimental studies (London 1986, 2008, 2015; Morgan and London 1987). However, the lack of diomignite as a component in spodumene-hosted inclusions negates the existence of a $\text{Li}_2\text{B}_4\text{O}_7$ -flux-rich silicate melt and its alleged role in the primary crystal-

lization of the Tanco pegmatite as described by London (2008).

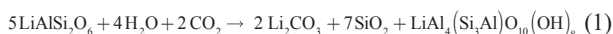
According to London et al. (1987):

Diomignite and the associated aluminosilicate daughter minerals represent the crystallization products of a late-stage hydrous borosilicate fluid that was entrapped principally by spodumene that formed as a result of the breakdown of petalite to spodumene + quartz.

These same crystal-rich inclusions were later reinterpreted to represent aliquots of flux-rich (12 mass% B₂O₃) boundary layer melt, whose composition is essentially identical to experimentally generated boron-rich (>10 mass% B₂O₃) boundary layers (London 2008).

The name diomignite was derived by London et al. (1987) from Homeric Greek *dios mignen*, meaning divine mix, in allusion to the fluxing properties of Li₂B₄O₇ on silicate-water systems. Its total absence in spodumene- and petalite-hosted inclusions, however, refutes the purported role of Li₂B₄O₇ in dramatic lowering of solidus temperatures, increasing silicate-H₂O miscibility, and enhancing the solubility of ore-forming incompatible lithophile elements in the Tanco pegmatite (London 1986). Boron in the form of boric acid is enriched in some aqueous fluid inclusions in quartz found within the core of the Tanco pegmatite, and some of these inclusions may contain sassolite (H₃BO₃) daughter crystals (Thomas and Davidson 2015). Similar boron-bearing aqueous fluid inclusions are reported in tourmaline-bearing pegmatites (Williams and Taylor 1996; Peretyazhko et al. 2000) and are generally interpreted to represent aqueous fluids that exsolved from the pegmatite melt. London (1985) argued that quartz-hosted aqueous and aqueous carbonic fluid inclusions in the Tanco are secondary in origin and are not representative of the medium from which the quartz was deposited. If this is correct, then the sassolite-bearing fluid inclusions in the quartz core do not represent a flux-rich melt. Furthermore, sassolite was not found within spodumene- or quartz-hosted inclusions in the intermediate zones in the Tanco pegmatite, and the typical concentration of boron in these inclusions is generally less than 1000 ppm (Der Channer and Spooner 1992; Paslawski et al. 2016). These results question whether the crystal-rich inclusions in spodumene are relatively flux-rich at all, and whether they actually represent the crystallized products of a trapped boundary layer melt.

Anderson (2013) has pointed out that *secondary* spodumene, formed by the isochemical breakdown of petalite, could not have trapped a boundary layer liquid that is spatially and temporally confined to crystal growth fronts during *primary* crystallization of the pegmatite. It is suggested that the mineral assemblage within these inclusions, consisting of quartz, cookeite, and zabuyelite (see supplemental material¹), formed from reaction 1 involving spodumene and an aqueous-carbonic fluid.



This hypothesis, which is being experimentally tested, is supported by the occurrence of numerous crystal-rich inclusions in healed fractures and cleavages.

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